

# Chapter 11

## Molecular Spectra

### 11.1 Introduction

The **line spectra** emitted from a gas discharge tube generally consist of a number of discrete lines. The origin of this line spectra lies in the atoms of different elements. The origin of line spectra can be understood with the help of **Bohr-Sommerfeld theory** and quantum mechanics.

There are other types of spectra emitted by substances in the **molecular state**. The molecules may contain two or more atoms. These molecular spectra appear as continuous bands under low dispersion and are known as **band spectra**. The band has a sharp intense edge on one side and is called **band head**. The intensity of the band gradually decreases as one moves towards the other side of it.

When a spectral band is observed through high resolving power instrument the spectral band is found to consist of **three-fold** structure as below :

- At the long wavelength side, a large number of lines are found to be crowded together. These lines are arranged in a regular fashion. Generally, the lines spread out from a fixed point in the band which is called the **band origin**.
- Several bands in the spectrum follow one another in a regular sequence and thus constitute a **group of bands**.
- The closely spaced different bands, because of their regular arrangement, form a **band system**. There may be more than one band system in a given molecular spectrum.

### 11.2 Category of Molecular Spectra

The band spectra of molecules may be divided into the following three classes :

- Rotational spectrum** : The rotational spectrum arises due to the radiation absorbed or emitted when a transition between two rotational energy levels occurs. During this transition the vibrational state of the molecules and the electronic configuration of the atoms remain unchanged.

The order of energy associated with the above transition is  $\sim 10^{-3}$  eV and thus the emitted radiation lies in the **far infrared** or **microwave region** of wavelength  $\lambda \sim 10^7$  Å. This wavelength is much longer than that of visible light.

- Rational-vibrational spectrum** : This spectrum arises due to radiation emitted or absorbed when a transition between two vibrational levels takes place while the electronic configuration of the atoms remains the same.

Under this condition rotational levels may or may not undergo a change. A **pure vibrational spectrum** is obtained if the rotational levels remain unchanged.

The transitional energy being  $\sim 0.1$  eV, the emitted radiation is in the **near infrared region** of wavelength  $\lambda \sim 10^5$  Å.

- (iii) **Electronic spectrum** : The electronic spectrum arises due to radiation emitted or absorbed when a transition between two electronic energy levels of an atom in a molecule takes place.

The wavelength of this spectrum ranges from 1000 to 7000 Å and hence lies in the visible or in the ultraviolet region.

### 11.3 Complexity of the Molecular Spectra

A molecule may have various allowed energy states. The transition between these energy states gives rise to the emission or absorption of a photon resulting in the molecular spectrum.

We consider two possible energy states of a system viz.,  $E_1$  and  $E_2$  as shown in Fig. 11.1.

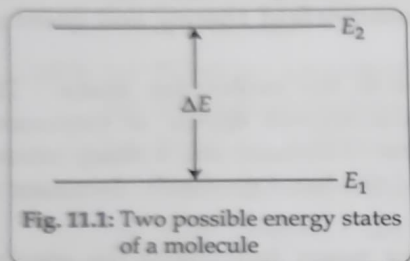


Fig. 11.1: Two possible energy states of a molecule

The transition can take place between the levels  $E_1$  and  $E_2$  provided the appropriate energy amount of energy  $\Delta E = E_2 - E_1$  can be either absorbed or emitted by the system. According to **Max Planck**, such absorbed or emitted energy can take the form of electromagnetic radiation whose frequency is given by

$$\nu = \frac{\Delta E}{h}.$$

If  $E_2 > E_1$ , then  $\nu = \frac{E_2 - E_1}{h}$ , energy will be absorbed and if  $E_1 > E_2$ , then  $\nu = \frac{E_1 - E_2}{h}$ , energy will be emitted.

The molecular spectra thus obtained is more complicated than that of an atom. This is because of the following facts :

- Since a molecule has many more degrees of freedom it has many more energy levels as compared to that of an atom.
- Since the electrons in a molecule do not move in a central force field, the method of separation of angular motion from the radial is not possible. Hence, the orbital angular momentum is not conserved. This makes it impossible to level the energy states with orbital quantum number.
- In a molecule the nuclei can rotate about its centre of mass or vibrate about their mean position of rest or execute complex type of motion including rotation and vibration. That is why solving Schrödinger equation of motion becomes extremely difficult for such a complicated system.

In view of the above impasse, simple models of molecules have been proposed with a view to explain the molecular spectra satisfactorily. **Max Born** and **J. R. Oppenheimer** suggested that, an approximate solution of Schrödinger equation can be obtained by neglecting the coupling between the different types of motion. Then to a first approximation the energy of a molecule may be expressed as

$$E = E_t + E_e + E_v + E_r. \quad (11.1)$$

The electronic energy  $E_e$  is of the order of a few electron-volts. The vibrational energy  $E_v \ll E_r$  and the rotational energy  $E_r < E_v$ .

Of these different energies the translational energy  $E_t$  is not quantised as the space for the translational motion is large enough compared to the molecular dimension and we are not interested in it, so neglected.

$$\therefore E = E_e + E_v + E_r \quad (11.2)$$

$E_e$ ,  $E_v$  and  $E_r$  are quantised.

Since  $E_e \gg E_v \gg E_r$ , with each electronic state, several vibrational states are associated and with each vibrational states again a number of rotational states are involved.

Apart from the rotational, vibrational and electronic spectra, a nucleus when placed in a magnetic field, can give different energy levels, called **nuclear Zeeman levels**. The **nuclear magnetic resonance spectrum** arises due to transitions between the nuclear Zeeman levels. In a magnetic field, electron spin gives rise to two levels corresponding to  $m_s = \frac{1}{2}$  and  $m_s = -\frac{1}{2}$ . The transition between these two levels leads to the **electron spin resonance**.

### 11.3.1 Electronic Energy ( $E_e$ )

To have an idea of the order of magnitude of electronic energy, let  $a$  be the separation between the nuclei of the two atoms of a molecule. According to the uncertainty principle, the momentum of the valence electron is  $p_e = \Delta p$ .

$$\text{Since } a\Delta p = \hbar, \Delta p = \frac{\hbar}{a}.$$

The kinetic energy of the electron is then of the order of

$$E_e = \frac{p_e^2}{2m_e} = \frac{\hbar^2}{2m_e a^2}. \quad (11.3)$$

Taking  $a \sim 1 \text{ \AA}$  and substituting the standard values of  $\hbar$  and  $m_e$ , we get  $E_e \sim 3.80 \text{ eV}$ . Hence,  $E_e$  comes out to be of the same order of magnitude as that of a valence electron in an atom.

### 11.3.2 Vibrational Energy ( $E_v$ )

If  $F$  be the binding force of the electron to the nuclei, then the nuclei are also bound to the electrons by an equal and opposite force. If  $F$  be simple harmonic, then  $F = -kx$ , where  $k$  is the force constant and  $x$  is the displacement from the mean position of rest.

If  $m_e$  and  $M$  be the masses of the electron and the nucleus respectively, then their angular frequencies of vibration are

$$\omega_e = \sqrt{\frac{k}{m_e}} \quad \text{and} \quad \omega_N = \sqrt{\frac{k}{M}} \quad \text{respectively.}$$

$$\text{Hence, } \frac{E_v}{E_e} = \frac{\hbar\omega_N}{\hbar\omega_e} = \sqrt{\frac{m_e}{M}}. \quad (11.4)$$

$$\text{But } \frac{m_e}{M} \sim 10^{-3} \text{ to } 10^{-5};$$

$$\therefore \frac{E_v}{E_e} \sim 10^{-2}.$$

$E_e \sim 1 \text{ eV}$  and this produces spectral lines in the visible or ultraviolet regions.

$E_v \sim 10^{-2} \times 1 = 10^{-2} \text{ eV}$ , which would produce spectral lines in the infrared region of the electromagnetic spectrum.

### 11.3.3 Rotational Energy ( $E_r$ )

We consider a diatomic molecule with two nuclei each of mass  $M$  and separated by a distance  $a$ , then the rotational energy of the molecule is

$$E_r = \frac{\hbar^2}{2I} = \frac{\hbar^2}{Ma^2}, \quad (11.5)$$

where,  $I = \frac{1}{2}Ma^2$  is the moment of inertia of the diatomic molecule about an axis perpendicular to the line joining the nuclei and passing through the centre of mass of the system.



$$\therefore \frac{E_r}{E_e} = \frac{\frac{h}{Ma^2}}{\frac{h^2}{2m_e a^2}} = \frac{2}{h} \left( \frac{m_e}{M} \right)$$

$$\text{or, } E_r = \frac{2}{h} \left( \frac{m_e}{M} \right) E_e.$$

Thus  $E_r$  of a nucleus is less than  $E_e$  by a factor  $\sim (m_e/m)$ . Also,  $E_r$  is less than  $E_v$  by a factor  $\sim \left(\frac{m_e}{M}\right)^{\frac{1}{2}}$ . So,  $E_r$  is  $\sim 10^{-3}$  eV or less and  $E_v$  is  $10^{-1}$  to  $10^{-2}$  eV, less than  $E_e$ .

(12.6)

## 11.4 Classification of Molecules

The rotation of a three-dimensional complex molecule can be described in terms of three principal moments of inertia,  $I_a$ ,  $I_b$  and  $I_c$ , where the axes are designed so that  $I_a < I_b < I_c$ .

The molecules are generally classified on the basis of the relative values of  $I_a$ ,  $I_b$  and  $I_c$  into four different classes as follows :

1. **Linear molecules** : In a linear molecule all the constituent atoms are arranged in a straight line as in HCN molecule (Fig. 11.2). The principal axes of rotation may be

(i) the molecular axis or  $a$ -axis,

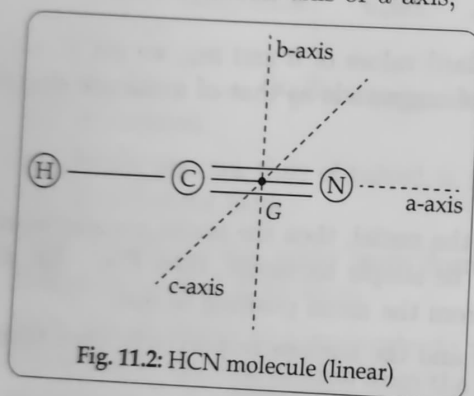


Fig. 11.2: HCN molecule (linear)

(ii) the  $b$ -axis in the plane of paper is perpendicular to  $a$ -axis and passing through the centre of gravity ( $G$ ) and

(iii) the  $c$ -axis perpendicular to both the axes  $a$  and  $b$  and passing through  $G$ . So,  $I_b = I_c$ , the moment of inertia for end-over-end rotation and  $I_a = 0$  as the mass of the atom is concentrated in the nucleus. So for linear molecules,  $I_a = 0$ ,  $I_b = I_c$ .

Examples : HCN, HCl,  $\text{CO}_2$ , etc.

2. **Symmetric tops** : All the three principal moments of inertia here are non-zero, two of them being equal [as in  $\text{CH}_3\text{Cl}$  molecule, Fig. (11.3)]. Here  $C$  has a tetrahedral coordination; the centre of gravity  $G$  is on  $\text{C-Cl}$  bond, the  $a$ -axis. The mutually perpendicular  $b$  and  $c$  axes pass through  $G$  and are in a plane normal to the  $a$ -axis. So,  $I_b = I_c$ . Further, if  $I_a < I_b = I_c$ , the symmetric top is **prolate**.

Examples :  $\text{CH}_3\text{Cl}$ ,  $\text{NH}_3$ , etc.

If  $I_a = I_b < I_c$  it is **oblate**.

Examples :  $\text{BCl}_3$ ,  $\text{BF}_3$ , etc.

3. **Spherical tops** : If  $I_a = I_b = I_c$ , i.e., the three principal axes are equal, then it is a spherical top.

Examples :  $\text{CCl}_4$ ,  $\text{CH}_4$ , etc.

4. **Asymmetric tops** : If  $I_a \neq I_b \neq I_c$ , the molecule is called an asymmetric top.

Examples :  $\text{H}_2\text{O}$ ,  $\text{CH}_3\text{OH}$ , etc. Majority of molecules belong to this class.

Here it is to be noted that, the spectra of linear diatomic molecules are relatively simpler, while those of asymmetric rotors are highly complex.

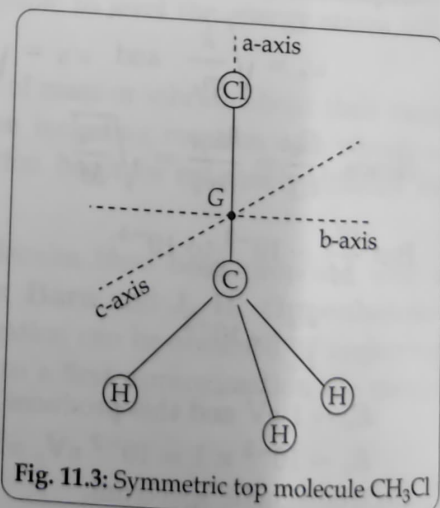


Fig. 11.3: Symmetric top molecule  $\text{CH}_3\text{Cl}$

## 11.5 Pure Rotational Energy Levels of Diatomic Molecules

If the two atoms of a diatomic molecule are supposed to be joined by a rigid rod so that the distance between them remains unchanged, then the electronic energy ( $E_e$ ) and the vibrational energy ( $E_v$ ) of the molecule remain unchanged as the molecule rotates as a whole. This model of the diatomic molecule is known as a **rigid rotar model**. It will be assumed that the rotation of the molecule takes place only about an axis perpendicular to the line joining the two atoms and the atoms are point masses.

If the two atoms of masses  $m_1$  and  $m_2$  rotate with an angular velocity  $\omega$  about an axis perpendicular to the line joining the two atoms passing through the centre of mass of the system [Fig. (11.4)], then the moment of inertia of the system about the axis is

$$I = m_1 r_1^2 + m_2 r_2^2, \quad (11.7)$$

where  $r_1$  and  $r_2$  are the distances from the centre of mass and  $R$  is the distance between the molecules.

Now, in the centre of mass coordinates

$$m_1 r_1 = m_2 r_2$$

$$\text{and } R = r_1 + r_2. \quad (11.8)$$

$$\text{From eqn (11.8), } r_1 = \left(\frac{m_2}{m_1}\right) r_2.$$

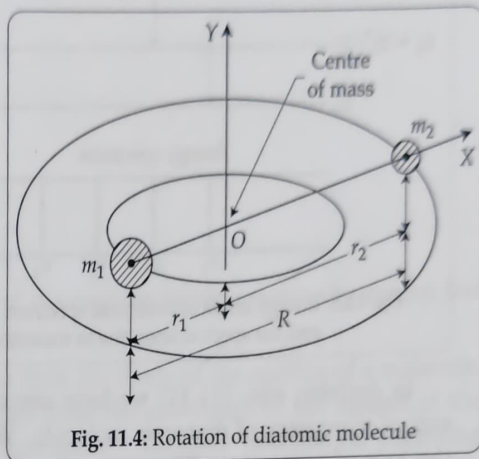


Fig. 11.4: Rotation of diatomic molecule

$$\therefore R = r_1 + r_2 = \frac{m_2}{m_1} r_2 + r_2 = r_2 \left( \frac{m_1 + m_2}{m_1} \right) \quad \text{or, } r_2 = \frac{m_1 R}{m_1 + m_2}$$

$$\text{Similarly, } r_1 = \frac{m_2 R}{m_1 + m_2}.$$

$$\begin{aligned} \therefore I &= \frac{m_1 m_2^2}{(m_1 + m_2)^2} R^2 + \frac{m_2 m_1^2}{(m_1 + m_2)^2} R^2 = m_1 m_2 \frac{m_1 + m_2}{(m_1 + m_2)^2} R^2 \\ &= \frac{m_1 m_2}{m_1 + m_2} R^2 = \mu R^2. \end{aligned} \quad (11.9)$$

where  $\mu = \frac{m_1 m_2}{m_1 + m_2}$  is the reduced mass of the system.

The kinetic energy of the molecule is

$$E = \frac{1}{2} I \omega^2 = \frac{1}{2I} (I\omega)^2 = \frac{J^2}{2I}, \quad (11.10)$$

where  $J = I\omega$ , the angular momentum of the system.

According to quantum mechanics, the orbital angular momentum is quantised and is given by

$$J = \sqrt{j(j+1)}\hbar,$$

where  $j$  is called the **rotational quantum number** which can take values 0, 1, 2, 3, .... The rotational energy levels of the diatomic molecules are given by

$$E_j = \frac{j(j+1)\hbar^2}{2I}$$

$$\text{and } F_j = BJ(J+1) = Bj(j+1), \quad (j = 0, 1, 2, \dots) \quad (11.11)$$

where  $B = \frac{\hbar^2}{2I}$ ,  $B$  is called the **rotational constant** for a diatomic molecule and  $F_j$  referred to as **rotational term value** having unit  $\text{m}^{-1}$ .

Thus, the molecules can have a discrete set of rotational energy levels as shown in Fig. 11.5.

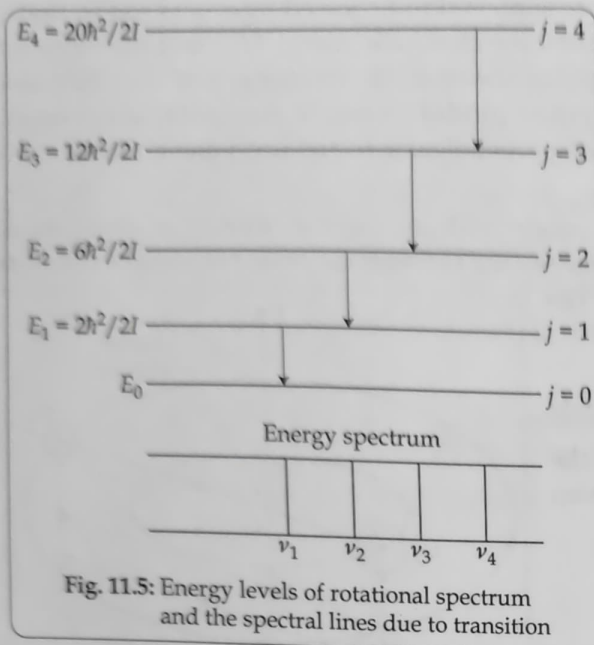


Fig. 11.5: Energy levels of rotational spectrum and the spectral lines due to transition

Eqn (11.11) shows that

- (i) A diatomic molecule cannot have any arbitrary value of energy. The energy is quantised and is limited by rotational quantum number  $J$ .
- (ii) The rotational energy depends upon moment of inertia, i.e., on the mass, shape and size of the molecule.

The difference between two rotational energy levels goes on increasing as  $j$  increases, e.g.,

$$E_1 - E_0 = \frac{2\hbar^2}{2I};$$

$$\text{but, } E_2 - E_1 = \frac{4\hbar^2}{8I}.$$

Thus  $(E_2 - E_1) > (E_1 - E_0)$ .

In deriving eqn. (11.11) we have assumed the rotation about an axis perpendicular to the axis of symmetry of diatomic molecule. We have neglected the rotation of the molecule about the axis of symmetry. The reason for the same is that the mass of the atom is concentrated almost entirely at its nucleus, the radius of which is  $\sim 10^{-4}$  of the radius of the atom as a whole. The main contribution to the moment of inertia of a diatomic molecule about the axis of symmetry comes from its electrons. Total mass of the electrons is about  $\frac{1}{4000}$  of the total molecular mass and these are concentrated in a region whose radius is about half the bond length  $R$ . As the allowed rotational energy levels are inversely proportional to  $I$ , rotation about the symmetry axis must involve energies of the order of  $10^4$  times the value of  $E_j$ . This means energies of several eV are involved for any rotation about the symmetry axis. The bond energies being of the same order of magnitude, the molecule will very likely dissociate under these conditions.

### 11.5.1 Rotational Spectra

#### Selection Rule

Due to transition between two rotational energy levels, rotational spectra of diatomic molecules arise. The selection rule for such a transition between rotational levels is

$$\Delta J = J_f - J_i = \pm 1, \quad (11.12)$$

where  $J_f$  and  $J_i$  refer to the final and initial energy levels respectively. That is transitions leading to a change in  $J$  by one unit are only allowed, the rest being forbidden.

The change in rotational energy in allowed transition is given by

$$\Delta E = E_{J+1} - E_J = \frac{2\hbar^2}{8\pi^2} (J+1) = \frac{\hbar^2}{I} (J+1).$$

But,  $E = h\nu$ .

$\therefore$  the photon involved in the rotational spectral line is given by

$$h\nu_J = E_J - E_{J-1} = \frac{\hbar^2}{2I} J[J+1 - (J-1)] = 2BJ.$$



$$\therefore \nu_J = \frac{2B}{h} J \quad (J = 1, 2, 3, \dots).$$

(11.13)

The spectrum has the frequencies,  $\nu_1 = \frac{2B}{h}$ ,  $\nu_2 = \frac{4B}{h}$ ,  $\nu_3 = \frac{6B}{h}$ .

The value of  $B$  can be determined from the experimental values of  $\nu$ .  $B$  can also be calculated from intermolecular distance and the atomic masses.

Now for,  $J = 0$ ,  $\nu_0 = 0$

$$J = 1, \nu_1 = \frac{2B}{h}$$

$$J = 2, \nu_2 = \frac{4B}{h}$$

$$J = 3, \nu_3 = \frac{6B}{h}$$

$$J = 4, \nu_4 = \frac{8B}{h}$$

$$\therefore \nu_2 - \nu_1 = \nu_3 - \nu_2 = \nu_4 - \nu_3 = \dots = \frac{2B}{h}.$$

Thus, the frequencies of rotational spectrum of diatomic molecule are equally spaced but the energy levels are not.

The importance of the rotational spectra is that from the study of the spectra of a molecule, its moment of inertia ( $I$ ) can be estimated and then from the knowledge of the masses of the constituent atoms the bond length ( $R$ ) can be determined. Valuable information regarding the **molecular structure** can be obtained from the discrete pure lines observed in gaseous substances. However, it is not easy to get such information for fluid.

The spacing between the consecutive rotational lines is thus independent of  $J$ , given by

$$\Delta \bar{\nu} = 2B = \frac{h}{2\pi I}.$$

The pure rotational spectral lines are thus equispaced. This is illustrated in Fig. 11.6, which shows pure rotational absorption spectrum of HF molecule. The wave number difference between the consecutive rotational lines is found to be  $\Delta \bar{\nu} = 4050 \text{ m}^{-1}$  in case of HF molecule.

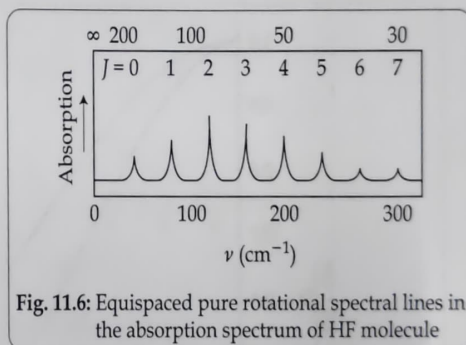


Fig. 11.6: Equispaced pure rotational spectral lines in the absorption spectrum of HF molecule

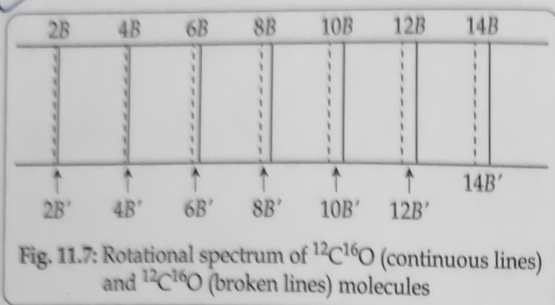
### 11.5.2 All Diatomic Molecules do not Exhibit Rotational Spectra. Why?

We know that rotation spectra arise from the transition between the rotational energy levels. Since the emission of radiation is due to the **rotation of electric dipole moment**, only the molecules having the electric dipole moment can absorb or emit electromagnetic radiation, and hence can exhibit rotational spectra.

The molecules like HCl or CO (heteronuclear) consisting of unlike atoms consist of unlike atoms possess permanent dipole moment as the centre of gravity of positive and negative charges do not coincide. For example, in HCl molecule an electron is transferred to Cl from H and the molecule takes the form  $\text{H}^+\text{Cl}^-$ . The centre of gravity of  $\text{H}^+$  and  $\text{Cl}^-$  does not coincide and an electric dipole is formed. The component of dipole moment along a fixed direction changes periodically as the molecule rotates giving rise to rotational spectra.

In case of symmetric (homonuclear) molecules consisting of like atoms viz.,  $N_2$ ,  $H_2$ ,  $O_2$ ,  $CO_2$  ( $O=C=O$ ) and  $CH_4$ , no such dipole moment is present and hence cannot emit or absorb electromagnetic radiation. Though the rotational levels exist in such atoms, transitions between them normally do not occur and hence rotation spectra are not observed. Thus, pure rotational spectrum can arise in case of polar molecules.

### 11.5.3 Isotope Effect

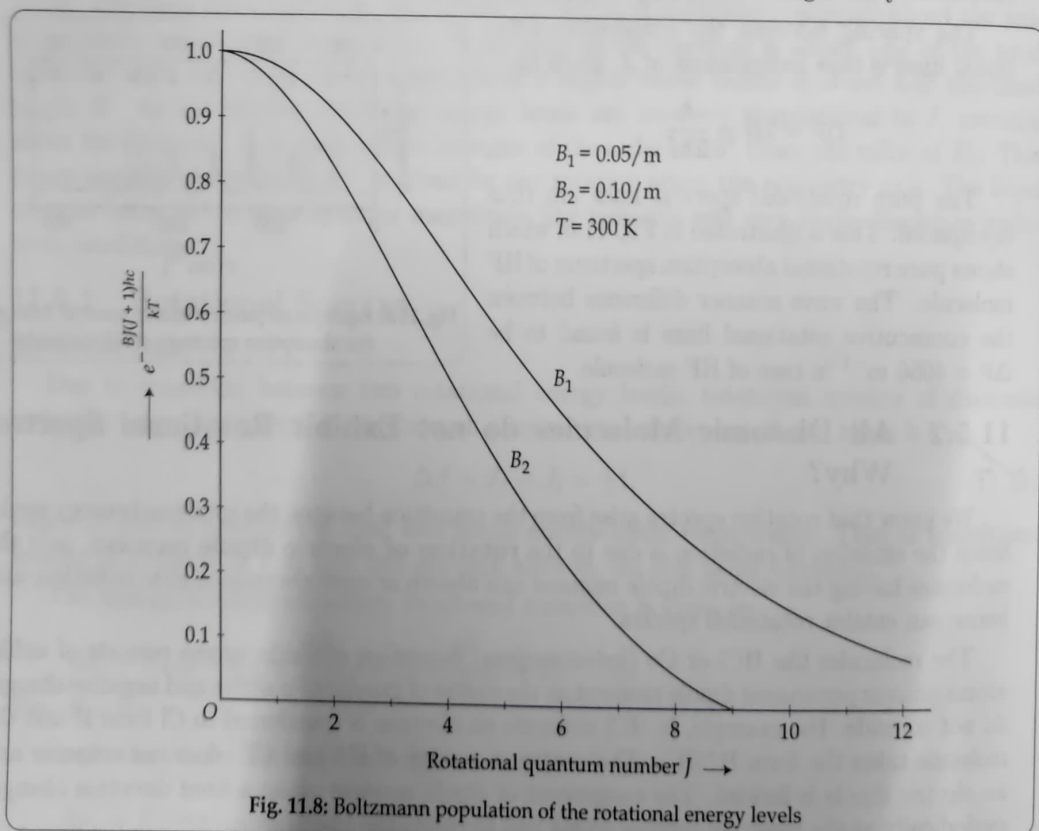


If an atom is replaced by its isotope, the electron charge distribution and hence the bond length remain unchanged. But as the mass of the nucleus changes, a change of  $I$  to  $I'$  and  $\nu$  to  $\nu'$  occurs. If  $I' > I$ , it leads to a positive value of  $\Delta\nu (= \nu - \nu')$ . The effect of  $^{13}C$  substituting  $^{12}C$  of  $^{12}C^{16}O$ , the **isotope shift** in rotational lines is shown in Fig. 11.7.

### 11.5.4 Intensities of Rotational Spectral Lines

We know that the transitions between the rotational levels are governed by the selection rule  $\Delta J = \pm 1$ . This means that transitions will take place between the rotational levels  $J = 0$  to  $J = 1$ ,  $J = 2$  to  $J = 3$  and so on. The relative probabilities of these transitions are determined by the following two factors :

- The Boltzman factor giving the relative numbers of molecules in the different initial rotational states.
- The degeneracy or the statistical weights of these states. The existence of two or more energy states having exactly the same energy is known as the degeneracy.





## 11.6 Vibrational Energy Levels of Diatomic Molecules

In the rigid rotor model of a diatomic molecule the vibration of two atoms along the line joining them has been neglected. But actually the atoms vibrate along the line joining them as if they are connected by a massless spring. The distance  $R$  between the atoms changes in a periodic manner about a mean value  $R_0$ . If the amplitude of vibration is small, then the vibration of the molecule may be assumed to be simple harmonic.

The variation of potential energy between the atoms with  $R$  is shown in Fig. 11.10. In equilibrium position the bond length of a molecule is  $R_0$ . The molecule can absorb the energy supplied to it through the vibration of the atoms in it.

Considering the vibration of the atoms around  $R_0$  to be small, the potential energy  $V(R)$  about  $R_0$  can be expanded by Taylor series as

$$V(R) = V(R_0) + \frac{1}{2}(R - R_0)^2 \times \left( \frac{d^2V(R)}{dR^2} \right)_{R=R_0}, \quad (11.18)$$

since,  $\left( \frac{dV(R)}{dR} \right)_{R=R_0} = 0$

as  $R_0$  represents the distance corresponding to the minimum potential energy. Putting  $(R - R_0) = x$ , we have

$$V(R) = V(R_0) + \frac{1}{2}V''(R_0)x^2. \quad (11.19)$$

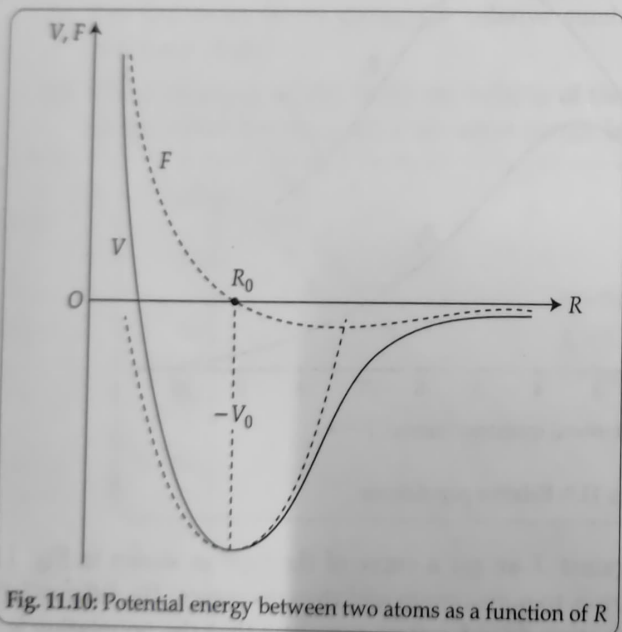


Fig. 11.10: Potential energy between two atoms as a function of  $R$

In eqn (11.19),  $V(R_0)$  is a constant and the second term  $\frac{1}{2}V''(R_0)x^2$  represents the potential energy of a simple harmonic oscillator with a force constant  $V''(R_0)$ . Calculating the slope of the potential energy curve at every point we can find out the force  $F = -\frac{\partial V}{\partial R}$ . The nature of variation of  $F(R)$  with  $R$  is shown in Fig. 11.10. It is evident from Fig. 11.10 that at

- (i)  $R = R_0$ ,  $V = -V_0$ , the minimum value of potential energy, the force  $F = 0$ ;
- (ii)  $R > R_0$ ,  $F$  is negative, i.e.  $F$  is attractive;
- (iii)  $R < R_0$ ,  $F$  is positive, i.e.,  $F$  is repulsive.

If the system be disturbed slightly, they will vibrate about the equilibrium position  $R_0$ . If the supplied energy is greater than  $-V_0$ , the atoms will fly apart and the molecule will be dissociated.

The potential energy curve can be approximated to a parabolic potential about  $R_0$  corresponding to a linear harmonic oscillator as shown by dotted curve in Fig. 11.10.

### 11.6.1 Vibrational Energy Levels

To find out the vibrational energy levels of a diatomic molecule, we consider two atoms  $a$  and  $b$  in a molecule having masses  $m_a$  and  $m_b$  respectively. The vibration of the molecule can be thought to be due to a spring of spring constant  $V''(R_0)$  between the atoms  $a$  and  $b$ .

If the motion be along  $X$ -direction, then let  $x_a$  and  $x_b$  be the distances of the atom  $a$  and  $b$  respectively from the origin  $O$ , then from Fig. 11.11,

$$x_b - x_a = R_0 + x \quad (11.20)$$

$$m_a \ddot{x}_a = V''(R_0)x \quad (11.21)$$

$$m_b \ddot{x}_b = -V''(R_0)x. \quad (11.22)$$

Multiplying eqns. (11.21) and (11.22) by  $m_b$  and  $m_a$  respectively and then subtracting the results, we get

$$m_a m_b (\ddot{x}_b - \ddot{x}_a) = -(m_a + m_b) V''(R_0)x. \quad (11.23)$$

Now, differentiating eqn (11.20) twice with respect to time  $t$ , we get

$$\ddot{x}_b - \ddot{x}_a = \ddot{x}. \quad (11.24)$$

From eqns (11.23) and (11.24), we get

$$\frac{m_a m_b}{m_a + m_b} \ddot{x} = -V''(R_0)x = \mu \ddot{x}, \quad (11.25)$$

where  $\mu = \frac{m_a m_b}{m_a + m_b}$  is the reduced mass of the system.

$$\text{or, } \mu \ddot{x} + V''(R_0)x = 0. \quad (11.26)$$

Eqn (11.26) represents a simple harmonic motion with frequency

$$\nu_0 = \frac{1}{2\pi} \left[ \frac{V''(R_0)}{\mu} \right]^{\frac{1}{2}}. \quad (11.27)$$

## 11.6.2 Quantum Mechanical Approach

Total vibrational energy of the molecule is

$$E_v = E_k + V = \frac{1}{2} \mu x^2 + \frac{1}{2} V''(R_0)x^2 = \frac{p^2}{2\mu}, \quad (11.28)$$

where  $p$  is the momentum of the system.

The Hamiltonian of the system is

$$\hat{H} = -\frac{p^2}{2\mu} + V = -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial x^2} + \frac{1}{2} \mu \omega_0^2 x^2. \quad (11.29)$$

The Schrödinger equation of the system can be written as

$$\hat{H}\psi = -\frac{\hbar^2}{2\mu} \frac{\partial^2 \psi}{\partial x^2} + \frac{1}{2} \mu \omega_0^2 x^2 \psi = E_v \psi. \quad (11.30)$$

The solution of eqn. (11.30) is

$$\psi = \left( \frac{\sqrt{\alpha}}{2^{\nu} \nu! \sqrt{\pi}} \right)^{\frac{1}{2}} e^{-\frac{\alpha x^2}{2}} H_{\nu}(\sqrt{\alpha}x), \quad (11.31)$$

where  $\alpha = \frac{m\omega_0}{\hbar}$ ,  $H_{\nu}(\sqrt{\alpha}x)$  is the Hermite polynomial of order  $\nu$ .

Putting  $\sqrt{\alpha}x = q$ , we get

$$H_{\nu}(q) = (-1)^{\nu} e^{q^2} \left( \frac{d}{dq} \right)^{\nu} e^{-q^2}. \quad (11.32)$$

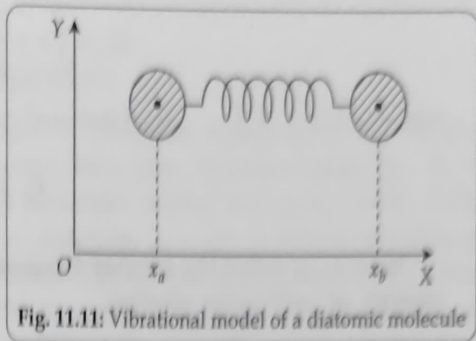


Fig. 11.11: Vibrational model of a diatomic molecule

The energy eigenvalues are given by

$$E_v = \left(v + \frac{1}{2}\right) \hbar \omega_0 = \left(v + \frac{1}{2}\right) h \nu_0, \quad (11.33)$$

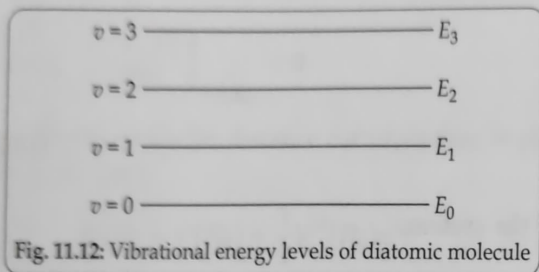
where  $v = 0, 1, 2, 3, \dots$ , the rotational quantum number. For  $v = 0$ , we get

$$E_0 = \frac{1}{2} \hbar \omega_0 = \frac{1}{2} h \nu_0. \quad (11.34)$$

Here,  $\nu_0$  is called the proper frequency of oscillation and  $E_0$  is called the zero point energy or null point energy.

### 11.6.3 Vibrational Spectra

The vibrational energy levels of the diatomic molecule corresponding to vibrational quantum numbers  $v = 0, 1, 3, \dots$  are shown in Fig. 11.12.



From equation (11.33),

$$\text{for } v = 0, E_v = E_0 = \frac{1}{2} h \nu_0$$

$$v = 1, E_v = E_1 = \frac{3}{2} h \nu_0$$

$$v = 2, E_v = E_2 = \frac{5}{2} h \nu_0$$

$$v = 3, E_v = E_3 = \frac{7}{2} h \nu_0.$$

$$\therefore E_1 - E_0 = E_2 - E_1 = E_3 - E_2 = h \nu_0.$$

Hence, the vibrational energy levels are equally spaced with energy interval  $h \nu_0$ .

### 11.6.4 Selection Rule

The selection rule can be stated as only those transition are allowed between vibrational energy levels, for which the vibrational quantum number  $v$  changes by one unit, i.e.,  $\Delta v = \pm 1$ .

This could be understood as below :

When electromagnetic radiation is incident on the oscillating dipole, it can absorb energy or emit energy of frequency  $\nu_0$  which is the frequency of oscillation of it. By absorbing a quantum of energy  $h \nu_0$ , the energy of oscillation of the dipole increases from  $(v + \frac{1}{2}) h \nu_0$  to  $(v + \frac{1}{2} + 1) h \nu_0$ . Similarly, it can emit energy  $h \nu_0$  at a time when its energy decreases from  $(v + \frac{1}{2}) h \nu_0$  to  $(v + \frac{1}{2} - 1) h \nu_0$ . This explains the justification of the selection rule,  $\Delta v = \pm 1$ .

### 11.6.5 Frequency of Lines in Vibrational Spectra

When a transition takes place from an energy level with quantum number  $(v + 1)$  to an energy level  $v$ , the energy of the emitted photon is

$$h \nu = E_{v+1} - E_v = \left(v + 1 + \frac{1}{2}\right) h \nu_0 - \left(v + \frac{1}{2}\right) h \nu_0 = h \nu_0.$$

$$\therefore \nu = \nu_0 = \frac{1}{2\pi} \sqrt{\frac{V''(R_0)}{\mu}}. \quad (11.35)$$

This is the frequency of the spectral line in vibrational emission spectra. It can be similarly shown that the frequency of the vibrational absorption spectra is also  $\nu_0$ . Hence, whatever be



the vibrational quantum number, the frequency of the radiation emitted or absorbed is equal to the classical frequency  $\nu_0$  of the oscillator.

## 11.7 Vibrational-Rotational Spectra

In liquids, due to interaction between the adjacent molecules, rotational motion of the molecules is not possible. That is why liquids cannot show pure rotational spectrum. In a gas or vapour the excitation energies involved in molecular motion are much smaller than those involved in vibration. So, the freely moving molecules in a gas or vapour are almost always rotating, irrespective of their vibrational states. The spectra of such molecules do not show isolated spectral lines due to transition between various vibrational states. Instead, a number of closely spaced rotational lines due to transitions between various rotational states of one vibrational level and the rotational states of other vibrational states are observed. These spectra when observed with a spectrometer appear as **broad streak** and are called **vibration rotation band**. It should be noted that like rotational spectra, **rotation-vibration spectra** are observed only for molecules having permanent dipole moment.

### 11.7.1 Vibration-Rotation Energy Levels

Since, the energies of rotation and vibration of a diatomic molecule are quite different, we may as a first approximation, consider that the diatomic molecule can execute rotations and vibrations quite independently. This is **Born-Oppenheimer approximation** according to which the combined rotational-vibrational energy is simply the sum of separate energies,  $E_J$  and  $E_v$ . The allowed energy levels are specified by two quantum numbers  $v$  and  $J$ . So, the total energy of the molecule is

$$E_{v,J} = E_v + E_J = \left(v + \frac{1}{2}\right) h\nu_0 + J(J+1) \frac{\hbar^2}{2I}, \quad (11.36)$$

where  $v = 0, 1, 2, \dots$  and  $J = 0, 1, 2, \dots$

When  $v = 0, J = 0$ , the total energy of the molecule is

$$E_{0,0} = \frac{1}{2} h\nu_0,$$

which is the minimum energy of the diatomic molecule and is called ground state energy. The higher energy values of the molecule, corresponding to  $v = 0, J = 1; v = 0, J = 2, \dots$  are called excited states.

The energy of the first excited state is

$$E_{0,1} = \frac{1}{2} h\nu_0 + \frac{\hbar^2}{I}.$$

The energy of the second excited state is

$$E_{0,2} = \frac{1}{2} h\nu_0 + \frac{3\hbar^2}{I}.$$

Similarly, the energies of the 3rd, 4th, ... excited state of the molecule are

$$E_{0,3} = \frac{1}{2} h\nu_0 + \frac{6\hbar^2}{I}$$

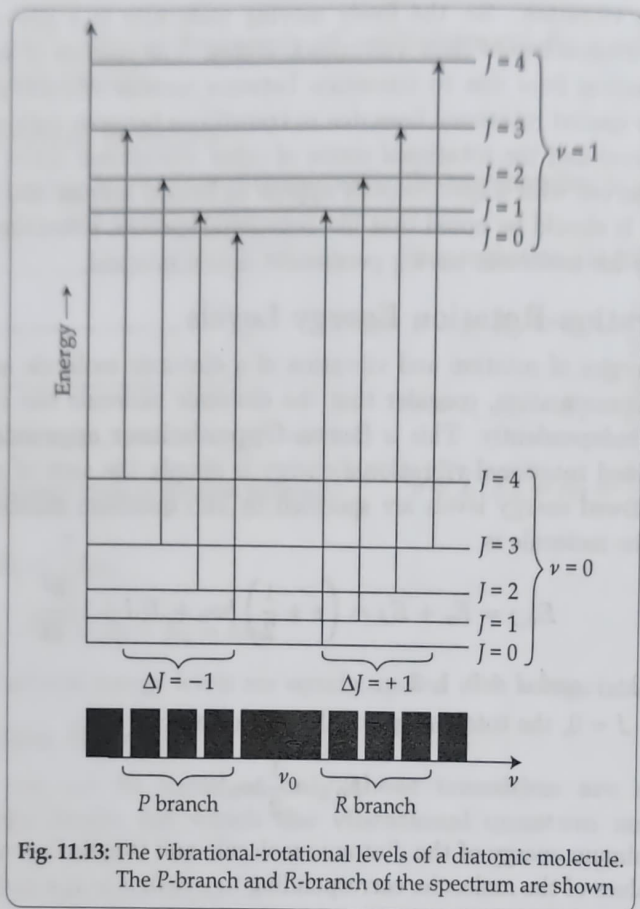
$$E_{0,4} = \frac{1}{2} h\nu_0 + \frac{10\hbar^2}{I} \text{ and so on.}$$

The allowed values of energies  $E_{0,0}; E_{0,1}; E_{0,2}, \dots$  are called **vibration-rotation energy levels** of the molecule.

The ground state vibrational energy  $\frac{1}{2}h\nu_0$  is greater than  $kT$ . Therefore, only a few molecules at room temperature are in an excited state. Further,  $E_v$  is very much greater than  $E_J$ . So, even at high temperatures only the vibrational states corresponding to  $v = 0$  and  $v = 1$  are excited.

### Energy level diagram

Fig. 11.13 shows  $J = 0, 1, 2, 3$  and  $4$  rotational levels of a diatomic molecule corresponding to two vibrational levels  $v = 0$  and  $v = 1$ . The spectral lines in absorption are also shown in the same figure.



### 11.7.2 The R-branch, Q-branch and P-branch

Due to selection rules  $\Delta v = \pm 1$  and  $\Delta J = \pm 1$  discrete lines are observed in both sides of the band origin at proper frequency  $\nu_0$ . The selection rules  $\Delta v = +1$  and  $\Delta v = -1$  correspond respectively for absorption and emission of spectral lines. The transition with  $J = 0$  is not allowed. The spectrum for higher frequency side i.e.,  $\nu > \nu_0$  is known as **R-branch**, while that on the lower frequency side, i.e.,  $\nu < \nu_0$  is known as the **P-branch**.

(1) **R-branch** : Here,  $\Delta J = +1$ , i.e., transitions are  $(J \rightarrow J+1)$ . The frequencies of the spectral lines in R-branch are given by

$$\begin{aligned} h\nu_R &= E_{1,J+1} \rightarrow E_{0,J} \\ &= \left[ \left( 1 + \frac{1}{2} \right) h\nu_0 + (J+1)(J+2) \frac{\hbar^2}{2I} \right] - \left[ \left( 0 + \frac{1}{2} \right) h\nu_0 + J(J+1) \frac{\hbar^2}{2I} \right] \\ &= h\nu_0 + (J+1) \frac{\hbar^2}{I} \end{aligned}$$

$$\text{or, } \nu_R = \nu_0 + (J+1) \frac{h}{4\pi^2 I}; \quad J = 0, 1, 2, \dots \quad (11.37)$$

(ii) **bio-chemistry** : Fluorescence excited by UV radiation is employed in the identification of minerals and compounds.

### 11.10.2 Phosphorescence

The selection rule for spin quantum number  $S$  in molecular spectra is the same as that in atomic spectra viz.,  $\Delta S = 0$ . This means no radiative transition takes place between singlet states  $S = 0$  and **triplet state with  $S = 1$** .

A molecule in the singlet ground state transits to the singlet excited state by absorbing a photon. The molecule in the singlet excited state may collide with other molecules and undergo radiationless transition to lower vibrational level. If this lower vibrational level in the singlet excited state coincides with one of the vibrational levels of the triplet excited state, then there is a certain probability that a shift to the triplet excited state with same vibrational energy may occur. The molecule may finally shift to  $v = 0$  level in the triplet state through collisions with other molecules [Fig. 11.18].

Though the transition from  $S = 1$  to  $S = 0$  level is forbidden, there is a little probability of radiative transition between these levels. Since, the half-life of such transitions is very large, the molecule may stay in the excited state for considerable long time. The radiation emitted from such molecular transitions usually takes after minutes or even hours after the absorption of the photon. This delayed radiation emitted due to molecular transition is called **phosphorescence**.

Materials which emit phosphorescence radiation are called phosphor. Phosphors have wide applications in fluorescent tubes and electronic appliances.

### 11.11 Raman Effect

Sir C.V. Raman, an Indian physicist, while studying the phenomenon of scattering of light (in 1920), observed that, when a beam of monochromatic light is passed through a transparent medium (solid, liquid or gas) and the scattered light at right angles to the incident beam is examined spectroscopically, it is found to contain lines of other frequencies in addition to that of incident light. This type of **incoherent scattering** was first discovered in liquids and is known as the **Raman effect**. For this important discovery Raman was awarded the **Nobel Prize in physics** in the year 1930.

The satellite lines on the low frequency side are called **Stokes lines** and those on the high frequency side, the **anti-Stokes lines**. All these satellite lines taken together are called **Raman lines** or **Raman spectrum** and the frequency shift from the parent line is called **Raman shift**. A typical Raman spectrum with Stokes and anti-Stokes lines is shown in Fig. 11.19.

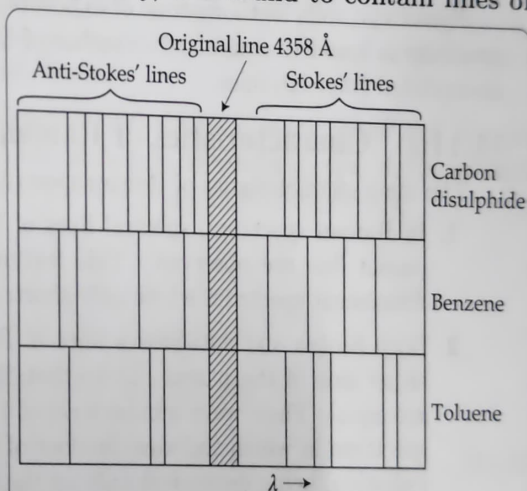


Fig. 11.19: A typical Raman spectrum showing Stokes' and anti-Stokes' lines

The apparatus used to study Raman effect in liquids is due to R. W. Wood, and is shown in Fig. 11.20.

It consists of a glass tube  $AB$  about 1 to 2 cm in diameter and 10 to 15 cm long containing the pure experimental liquid free from dust and air bubbles. The tube is closed at one end by an optically plane glass plate which forms the window  $W$  and the other end is drawn into the shape of a horn  $H$  and blackened on the outside. It is known as the **Raman tube**.



Light from a mercury arc source  $S$  is first passed through a suitable filter  $F$  which allows only monochromatic radiation of wavelength  $\lambda = 4358 \text{ \AA}$  to pass through. The tube is surrounded by a water jacket  $J$  through which cold water is circulated to prevent overheating of the liquid due to the proximity of the mercury arc. A semi-cylindrical polished aluminium reflector  $R$  is used to further increase the intensity of illumination.

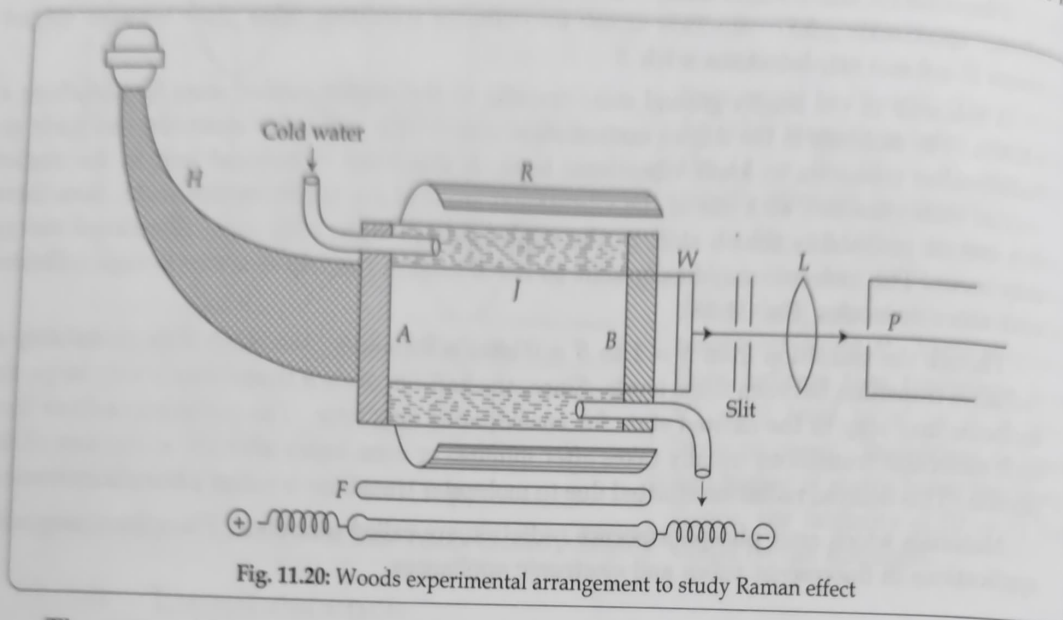


Fig. 11.20: Woods experimental arrangement to study Raman effect

The scattered light coming out of the window  $W$  is focussed on the slit of the spectrograph  $P$  with the help of a lens  $L$  in front of the window. The spectrograph is carefully aligned along the axis of the Raman tube and screened from the direct rays from  $S$ . The spectrograph is of high light gathering power and a special prism of high resolution. The spectrum is photographed by a short focus camera.

By using a sufficient long time of exposure, then on developing the photo plate, the Raman spectrum is found to consist of a number of Stokes lines, a few anti-Stokes lines and a strong un-modified Rayleigh lines.

### 11.11.1 Characteristics of Raman Lines

The main characteristics of Raman spectrum are enumerated below :

1. In Raman spectrum, spectral lines of both lower and higher frequencies than that of parent line are observed. This feature distinguishes Raman spectrum from that of fluorescent spectrum where only shorter frequency lines (Stokes lines) are observed.
2. Both Stokes and anti-Stokes lines in Raman spectrum are symmetrically situated on either side of the parent line so that their frequency differences from the parent lines are equal. Their wave numbers depend on that of the parent line unlike in fluorescent spectrum in which the wave number of Stokes line is independent of that of the parent radiation, being dependent only on the fluorescent material.
3. The frequency difference between the Raman lines depends on the nature of the scatterer but is independent on the frequency of the exciting radiation.

If  $\nu_0$  be the frequency of the exciting radiation and  $\nu_1$  and  $\nu_2$  that of the Stokes and anti-Stokes lines, then

$$\Delta\nu = \nu_0 - \nu_1 \quad (\text{for Stokes lines})$$

$$\text{and } \Delta\nu = \nu_2 - \nu_0 \quad (\text{for anti-Stokes lines}).$$

These differences in frequencies are usually known as Raman frequencies.

4. The frequency shifts are equal to the frequencies of the infrared absorption band or equal to the differences of the frequencies.

For instance, if benzene is irradiated by mercury lines of wave numbers  $27354\text{ cm}^{-1}$  and  $27290\text{ cm}^{-1}$ , the scattered lines are found to have wave numbers  $24294\text{ cm}^{-1}$  and  $24231\text{ cm}^{-1}$ , the scattered lines are found to have wave numbers  $24294\text{ cm}^{-1}$  and  $24231\text{ cm}^{-1}$ , respectively.

5. The intensities of Raman lines are  $\sim 1\%$  of that of parent lines in solids. For liquids and gases, it is still smaller. The Stokes lines are always more intense than the anti-Stokes lines. With the increase of temperature, the intensities of anti-Stokes lines increase to some extent.
6. The Raman lines are polarised. The different lines exhibit different degrees of polarisation.
7. There is no simple relationship between intensity ( $I$ ) and wavelength ( $\lambda$ ) in Raman scattering whereas in Rayleigh scattering the relation is  $I \propto \frac{1}{\lambda^4}$ . Thus, Raman scattering is basically different from fluorescent scattering.

### 11.11.2 Quantum Theory of Raman Effect

✓ According to quantum theory, a photon of frequency  $\nu$  has energy  $h\nu$ , where  $h$  is the Planck's constant. When a photon of energy  $h\nu$  is incident on a molecule of solid, liquid or gas, the following three processes may occur :

- The photon may collide with the molecule elastically and scatter without any change in energy and hence frequency. This explains the presence of **unmodified line** in the Raman spectrum.
- The photon may collide in such a way that a small fraction of its energy is transferred to the molecule. As a result, the photon is scattered with reduced energy or frequency and we get the **Stokes lines**.
- The photon may collide with a molecule in the excited state and gain some energy from the molecule. Then the energy and hence the frequency of the scattered photon is increased giving rise to the **anti-Stokes lines**.

Now let a photon of energy  $h\nu$  collide with a molecule of kinetic energy  $\frac{1}{2}mv^2$  and intrinsic energy  $E$ . If  $\nu_1$  be the frequency of the scattered photon,  $v_1$ , the velocity and  $E$ , the intrinsic energy of the molecule after collision, then from the law of conservation of energy,

$$h\nu + \left(\frac{1}{2}mv^2 + E\right) = h\nu_1 + \left(\frac{1}{2}mv_1^2 + E_1\right).$$

If there is no change in kinetic energy, i.e.,  $\frac{1}{2}mv^2 = \frac{1}{2}mv_1^2$ , then

$$h\nu + E = h\nu_1 + E_1 \quad \text{or,} \quad h\nu = h\nu_1 + (E_1 - E) = h\nu_1 + \Delta E$$

$$\text{or,} \quad \nu = \nu_1 + \frac{\Delta E}{h}. \quad (11.42)$$

**Stokes lines :** If the collision of the photon with the molecule is such that the molecule gains some energy from the photon, then the molecule goes from lower energy  $E$  to higher energy  $E_1$  and  $(E_1 - E)$  is positive. Then from eqn (11.42),

$$\nu_1 = \nu - \frac{\Delta E}{h}$$

$$\text{or,} \quad \nu_1 = \nu - \Delta\nu, \quad (11.43)$$

$$\text{where } \Delta\nu = \frac{\Delta E}{h}.$$

Thus, the frequency of the scattered photon ( $\nu_1$ ) is less than that of the incident photon. This explains the origin of the **Stokes line** in Raman spectra.

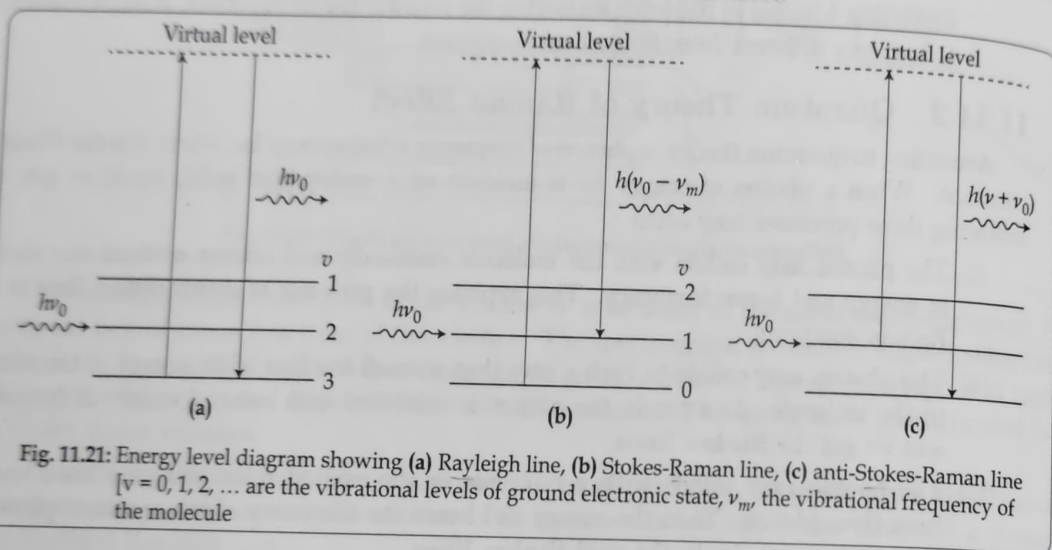
**Anti-Stokes lines :** When the photon collides with the molecules in the excited state, then the photon gains some energy from the molecule. The molecule then goes from higher energy  $E$  to lower energy state  $E_1$  and  $\Delta E = (E_1 - E)$  is negative, i.e.,  $\Delta E$  is negative.

From eqn. (11.41),

$$\nu_1 = \nu + \frac{\Delta E}{h} = \nu + \Delta\nu. \quad (11.44)$$

Since, the frequency of the scattered photon is greater than that of the incident photon, anti-Stokes lines appear in the Raman spectrum.

The origin of the Raman lines can thus be explained in a simple and straightforward way from the quantum theory. The different processes giving rise to Rayleigh, Stokes and anti-Stokes lines are illustrated in Fig. 11.21. To note that, Raman effect also occurs in atomic spectra but Raman effect in relation to molecules is of more interest.



**N.B. 1.** In Fig. 11.21 the virtual state is not a stationary state, for if it is one, any monochromatic incident frequency cannot be used.

**2.** The classical electromagnetic theory can also explain the origin of Raman lines but it fails to explain the intensity or the polarisation of Raman lines. Therefore, the classical theory of Raman effect will not be discussed here.

The frequency difference  $\Delta\nu$  of Stokes and anti-Stokes lines from the parent line is given by

$$\Delta\nu = \nu' - \nu_0 = \frac{(E_1 - E_2)}{h}.$$

So,  $\Delta\nu$  depends on the energy states of the molecule and not on the frequency of the parent line.

Applying quantum principle,

$$E_1 \sim E_2 = nh\nu_m, \quad n = 1, 2, 3, \dots$$

where  $\nu_m$  is the characteristic frequency of the molecule.

$$\therefore \nu' = \nu_0 \pm \nu_m, \quad \text{when } n = 1. \quad (11.45)$$

This explains the symmetrical distribution of the Raman lines about the incident line at intervals corresponding to the characteristic frequency of the scatterer and to its infrared absorption line.



### 11.11.3 Intensities of Raman Lines

The transition probability of atoms, molecules, etc. responsible for the origin of the spectral line is the key factor which determines the intensity of the same line. If the transition probability is more, then the intensity of the corresponding spectral line will be more.

According to Maxwell-Boltzmann statistics, the number of molecules in the energy level  $E$  is given by

$$n = n_0 e^{-E/kT}, \quad (11.46)$$

where  $k$  is the Boltzmann constant and  $T$  is the absolute temperature.

From eqn. (11.46), it is evident that  $n$  decreases as  $E$  increases. When  $E = 0$ ,  $n = n_0 = (n)_{\max}$ , i.e., the number of molecules is the maximum in the ground state corresponding to  $E = 0$  and decreases as  $E$  increases. The ratio of the number of molecules in the excited state to that in the ground state is

$$\frac{n}{n_0} = e^{-E/kT}. \quad (11.47)$$

At  $T = 300$  K, the rotational state energy  $E_r$ , just above the ground state is

$$E_r \sim 5 \times 10^{-3} \text{ eV}.$$

At  $T = 300$  K,

$$kT = \frac{1.38 \times 10^{-23} \times 300}{1.6 \times 10^{-19}} = 2.6 \times 10^{-2} \text{ eV}.$$

$$\therefore E_r \ll kT$$

$$\text{and } \frac{n_r}{n_0} = e^{-\frac{E_r}{kT}} = e^{\left(\frac{-5 \times 10^{-3}}{2.6 \times 10^{-2}}\right)} \simeq e^{-0.2} = 0.82. \quad (11.48)$$

So at room temperature ( $T = 300$  K) nearly 82% of the molecules are in the low-lying excited rotational states.

Again, the energy of the low-lying vibrational level,

$$E_v = 0.36, \quad \therefore E_v \gg kT$$

$$\therefore \frac{n_v}{n_0} = e^{-\frac{E_v}{kT}} = e^{\left(\frac{-36 \times 10^{-2}}{2.6 \times 10^{-2}}\right)} = e^{-13.85} = 9.7 \times 10^{-7}. \quad (11.49)$$

Thus, the number of molecules in the low-lying vibrational state is only  $9.7 \times 10^{-5}\%$  which is very small.

Since at  $T = 300$  K, the number of molecules ( $n_0$ ) in the ground state is the maximum, the transition probability from the ground state to the higher excited state is greater than the transition probability from higher state to the ground state. This explains the greater intensity of the Stokes lines than the anti-Stokes lines. The intensity of the anti-Stokes lines of rotational Raman spectrum may increase with the increase of  $T$ .

At any temperature the ratio of the intensity of anti-Stokes and Stokes lines is

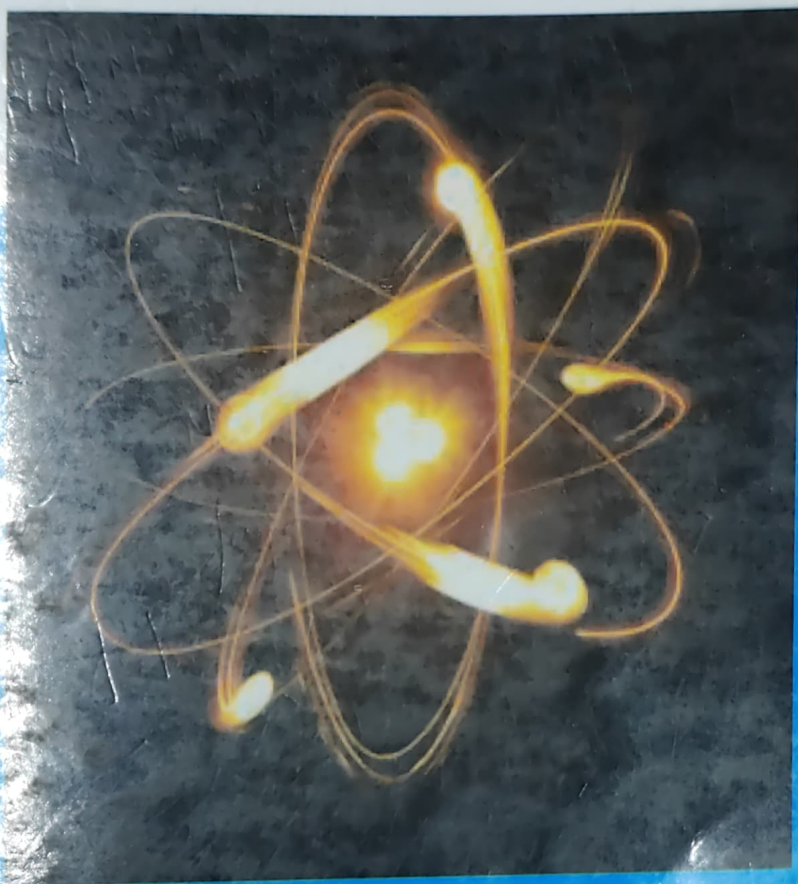
$$\frac{I_A}{I_S} = e^{-(ch\Delta\bar{\nu}/kT)}. \quad (11.50)$$

The ratio  $\frac{I_A}{I_S}$  is the same as the ratio of number of molecules in the excited state to that in the ground state.

### 11.11.4 Rotational Structure of Raman Spectra

The Raman lines, viz., Stokes and anti-Stokes lines, arise due to the transition of the molecules between vibrational and rotational levels. If the vibrational state of molecule undergoes

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